PB84-177849

Partitioning of Toxic Trace Metals between Solid and Liquid Phases in the Great Lakes

Cranbrook Inst. of Science, Bloomfield Hills, MI

Prepared for

Environmental Research Lab.-Duluth, MN

Apr 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-177849

EPA-600/D-84-098
April 1984

PARTITIONING OF TOXIC TRACE METALS BETWEEN SOLID AND LIQUID PHASES IN THE GREAT LAKES

by

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EPA Grant
CR 804442

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U.S. ENVIRONMENTAL PROTECTION AGENCY
DULUTH, MN 55804

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/D-84-098	2.	3. RECIPIENT'S ACCESSION NO. PB84 177849
4. TITLE AND SUBTITLE Partitioning of Toxic Trace Metals Between Solid and Liquid Phases in the Great Lakes		5. REPORT DATE 1984 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) K. R. Rygwelski		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Cranbrook Institute of Science 500 Lone Pine Road Bloomfield Hills, MI 48103		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. CR 804442
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Duluth, MN 55804		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA-600/03
15. SUPPLEMENTARY NOTES		

16. ABSTRACT The interaction between particulate matter and trace metal species in the water column plays an important role in metals transport and fate throughout the Great Lakes environment. Where there is strong sorption of a metal by particulates and settling is involved, then the metal should not be regarded as a conservative substance in the water column. Dolan and Bierman (1982) modeled the transport of trace metals in Saginaw Bay, Lake Huron, and found that a large percentage of the cadmium, lead and zinc were lost to the sediments via metal association with particulates suspended in water. Enrichment of cadmium, lead, zinc and copper was found in surface sediments of Lakes Superior and Huron by Kemp et al. (1978) and of Lakes Ontario and Erie by Kemp and Thomas (1976). Dredging operations and water turbulence can resuspend these particulates and sorbed metals may be subsequently released again to the water column. Other studies have indicated that trace metal magnification in organisms can occur both through the food chain via particulates (bioaccumulation) and directly from the water via sorption of membrane surfaces (bioconcentration). Phillips and Russo (1978) prepared an extensive review of literature on the biomagnification of twenty-one trace metals in fishes and aquatic invertebrates. The availability of trace metals to aquatic organisms in the Great Lakes can best be understood, at least in general terms, through the phenomenon of solid-liquid partitioning. The following represents a brief review of partition theory and published data of trace metal partitioning in Saginaw Bay conducted during 1976-1978.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS (This Report) unclassified	21. NO. OF PAGES 25
	20. SECURITY CLASS (This page) unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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1. Introduction

The interaction between particulate matter and trace metal species in the water column plays an important role in metals transport and fate throughout the Great Lakes environment. Where there is strong sorption of a metal by particulates and settling is involved, then the metal should not be regarded as a conservative substance in the water column. Dolan and Bierman (1982) modeled the transport of trace metals in Saginaw Bay, Lake Huron, and found that a large percentage of the cadmium, lead and zinc were lost to the sediments via metal association with particulates suspended in water. Enrichment of cadmium, lead, zinc and copper was found in surface sediments of Lakes Superior and Huron by Kemp et al. (1978) and of Lakes Ontario and Erie by Kemp and Thomas (1976). Dredging operations and water turbulence can resuspend these particulates and sorbed metals may be subsequently released again to the water column. Other studies have indicated that trace metal magnification in organisms can occur both through the food chain via particulates (bioaccumulation) and directly from the water via sorption on membrane surfaces (bioconcentration). Phillips and Russo (1978) prepared an extensive review of literature on the biomagnification of twenty-one trace metals in fishes and aquatic invertebrates. The availability of trace metals to aquatic organisms in the Great Lakes can best be understood, at least in general terms, through the phenomenon of solid-liquid partitioning. The following represents a brief review of partition theory and published data, including results of studies by Cranbrook of trace metal partitioning in Saginaw Bay conducted during 1976-1978.

2. Adsorption

Much research has indicated that adsorption processes are important in regulating metals partitioning between suspended particles and water [Gardiner (1974); O'Conner and Connolly (1980); Oakley et al. (1981)]. Chemisorption and physical adsorption processes were defined by Smith (1981). Physical adsorption is characterized by weak attraction of the metal solute to the solid surface, by high reversibility, and by nonspecificity of sorbants. Chemisorption, on the other hand, is highly dependent on the nature of the solids, often occurs irreversibly, and forms relatively strong bonds of the type occurring between atoms in molecules. Weber (1972) also included ion exchange as an adsorptive process. All three types may occur simultaneously in natural waters, and often the mechanisms interact.

2.1 Adsorption and Metal Species

The simple metal ion in the aquatic system is subject to numerous chemical reactions, such as precipitation, redox reactions, and complexation with various ligands. As a result, a wide variety of metal species exists in natural water systems. This complicates the adsorption process considerably since each of these metal species in solution can have different adsorption mechanisms. Davis and Leckie (1978) found that the percent of Cu^{2+} adsorbed to amorphous iron oxide increased rapidly as the pH of the water increased. They theorized that the easily adsorbed $CuOH^{1+}$ species was responsible for the higher adsorption of Cu^{2+} in the higher pH range. Also, they found that Cu^{2+} adsorption increased in the presence of the organic ligands, glutamic acid and 2,3-pyrazinedicarboxylic acid. Picolinic acid was found to inhibit adsorption.

Theoretical adsorption models help to deal with the great complexity of natural systems. Vuceta and Morgan (1978) modeled the equilibrium distribution of trace metals in fresh water. They predicted that when complexing agents or ligands are absent or in low concentration, then Cu^{2+} will be substantially removed from solution by adsorption onto particles. However, when complexing agents are abundant then the adsorbed metal should be totally or partially released from particles. They theorized that Zn^{2+} exists in solution as a free ion, but as the adsorbent surface area or organic ligand concentration increases then some adsorption and complexation does occur. They predicted that the distribution of Pb^{2+} between aqueous and adsorbed species would primarily depend on the total surface area of the adsorbent. Huang et al. (1977) reported the effects of pH on trace metal adsorption. Using hydrous oxides and soils, adsorption abruptly increased in the pH ranges of 6 to 7 (cadmium) and 5 to 6 (lead, copper, zinc).

Due to the generally low levels of trace metals in natural waters it is often very difficult to determine the concentrations of various metal species present. For this reason, data on trace metal species or even total metals in fresh water systems are scarce, particularly in open waters of the Great Lakes where concentrations are very low.

2.2 Adsorption and Solids Composition

The nature of the adsorbent is also an important factor in adsorptive processes. A number of laboratory studies have been designed to determine the types of solids which act as good trace metal adsorbents. Gardiner (1974) found that humic materials in river mud are largely responsible for adsorption of cadmium. Concentration factors for different muds varied between 5,000 and 50,000. Oakley et al. (1981) used an equilibrium adsorp-

tion model to predict adsorption of copper and cadmium onto artificial geochemical materials in seawater. They concluded that the clay fraction was a major sink for copper and cadmium. Adsorption constants were calculated to be much higher for copper than for cadmium.

3. Sorption: A Combination of Adsorption and Absorption

Some of the variables affecting adsorption onto inert particles have been discussed. The accumulation of metals in the living component of suspended solids is further complicated by absorption. The term sorption has been used to describe this combination of adsorption and absorption [Weber (1972)].

The effect of various inorganic and organic chemicals in the water on trace metal sorption by a given algal or zooplankton species has been studied by Poldoski (1979). He found that in high concentrations of humic acid, pyrophosphate, or aminopolycarboxylic acids, complexation was effective in reducing cadmium uptake by *Daphnia magna*. He demonstrated that raising the calcium concentration in Lake Superior water five times above the baseline level resulted in a one-third lower uptake of cadmium during an exposure of two days. In the presence of diethyldithiocarbamate, the biomagnification of total cadmium was greater than uptake of the free cadmium ion alone. Keeney *et al.* (1976) showed that the bioconcentration factor (ratio of metal content in alga to metal concentration in water) in *Cladophora glomerata* was reasonably constant. Two sites in Lake Ontario were chosen to study the concentration factors in *Cladophora glomerata*. The [bioconcentration factors]/10^3 in Lake Ontario (Deadman Bay) were 2.9, 49, 16 and 2.2, and in Lake Ontario (Main Duck) they were 1.0, 18, 20, and 1.9 for zinc, cadmium, lead, and copper, respectively.

Sorption also seems to be species specific for algae or zooplankton. Conway and Williams (1979) measured the sorption of cadmium by two diatom species of the Great Lakes, Asterionella formosa and Fragilaria crotonensis. Initially, both species rapidly sorbed cadmium; however, the cellular cadmium content of A. formosa was about three times that of F. crotonensis. They concluded that the higher concentration in A. formosa was due to active uptake of cadmium. The initial rate of cadmium desorption was 10-100 times greater than the final rate. Milne and Dickman (1977) found that both attached and planktonic algae significantly concentrated lead when grown over lead contaminated sediments in snow dump areas in Ottawa. No differentiation was made here between adsorption and absorption.

4. Adsorption Isotherms

A number of adsorption isotherms have been used to characterize and simplify the sorption of dissolved metal species by complex mixtures of solid surfaces. The Langmuir, linear, and Freundlich isotherms have been applied to solid-liquid partitioning in sediments, soils, and suspended solids in water. The important assumptions for the Langmuir isotherm are constant activity of surface sites, no interaction between adsorbed metal species, all adsorption occurring by the same mechanism and confined to one complete monomolecular layer on the surface.

At equilibrium then:

$$(1) \qquad C = \frac{K_c C_m C_\ell}{1 + K_c C_\ell} \qquad \text{[Smith (1981)]}$$

where K_c = equilibrium constant

C_m = concentration of trace metal within a complete monomolecular layer on the surface

C_L = concentration of metal dissolved in water

C = adsorbed concentration.

In dilute systems where C_L is small then (1) becomes a linear adsorption isotherm:

(2) $$C = K_C C_m C_L = \P C_L$$

where ¶ is often defined as the partition coefficient (O'Conner and Connolly, 1980).

The Freundlich isotherm is defined as:

(3) $$C = C_m k C_L^{1/n}$$

where n has a value greater than unity

k is a constant.

Combining constants then:

(4) $$C = K C_L^{1/n}$$

These adsorption isotherms have been successfully applied to solid-liquid partitioning of trace metals in natural systems. Even though all the assumptions described for the Langmuir isotherm may not be met, the basic assumptions of a finite adsorption time and dynamic equilibrium between rates of adsorption and desorption (on which the Langmuir isotherm is based) are sound. In a complex mixture of solids it may not be possible to determine K_C and C_m in Equation (2), but the constant ¶ may be determined from the linear portion of the adsorption isotherm [Weber (1972)]. One requirement is that the adsorptive equilibrium be achieved rapidly and maintained. Reasoning that the concentrations of trace metals are usually low relative to

the adsorptive capacity of solids, O'Conner and Connolly (1980) applied Equation (2) to various solutes. For a given solute they found that ¶ can vary depending on the nature and concentration of adsorbent.

The two constants in Equation (4) make the Freundlich isotherm flexible; often constants can be chosen so that experimental data can be curve-fitted over a reasonable range of concentrations. Despite this curve-fitting capability, Travis and Etnier (1981) advise against extrapolating beyond experimental points in the curve. Gardiner (1974) preferred to characterize adsorption of cadmium onto mud using the Langmuir isotherm, since the composition of solids in mud is complex and it is therefore not possible to determine both constant K and n in Equation (4).

If conditions allow the use of Equation (2) then C_ℓ and C must be determined. One method is to measure the total and dissolved metal in the water. Dissolved metal is operationally defined as that portion which passes through a .45 μm porosity filter. The partition coefficient then becomes:

$$(5) \qquad ¶ = \frac{\frac{T - C_\ell}{SS}}{C_\ell} = C/C_\ell$$

where SS is the suspended solids concentration.

T is the total metal concentration in water.

4.1 Applications

The widely accepted filter pore size (.45 μm) for obtaining a dissolved metal sample (C_ℓ) may not be appropriate for all metals in all types of water. Poldoski (1979) suggested that the .1 μm pore size filter may be more appropriate for measuring C_ℓ in some water types. In the presence of complexing ligands, humic acid and diethyldithiocarbamate, he noted decreasing

concentrations of cadmium in C_ℓ as he decreased pore sizes from .45 μm to .1 μm. Copper concentrations showed no pore size dependence [Poldoski (1974)].

Problems can occur in using Equation (5) when suspended solids concentrations are low. Under these conditions the measured values of $T-C_\ell$ are often zero or negative. This results in being negative, which is not possible. When the population of solids >.45 μm is low, then the fraction of particulate metal in the water is very small. The precision of the analytical method used then may not be sufficient to properly differentiate between T and C_ℓ.

There are alternative ways to determine ¶ when the suspended solids concentrations are low. The partition coefficient may be determined by concentrating the solids in the sample with a continuous flow centrifuge [Nriagu et al. (1980)]. Relatively large quantities of suspended solids can be collected by this means because of the huge volumes of water that can be processed. Filtering sufficient water and analyzing the solids collected is another approach.

Assuming Equation (2) still holds, ¶ then becomes:

$$(6) \qquad ¶ = \frac{\text{weight of metal in solids/volume filtered}}{\frac{SS}{C_\ell}}$$

5. Partition Measurements

Due to the complexities of sorption phenomena and the limitations of sampling and analytical methodology, little information exists on metal partitioning between solid and liquid phases in the Great Lakes. Many laboratories lack instruments sensitive enough to analyze open lake waters for trace metals. Some data do exist, but due to the varied nature of sus-

pended solids and chemistry of lake water, there are problems in comparing partition data from different areas.

5.1 Form of Metal in Natural Water

Several studies have focused on the extent to which various metals associate with suspended solids. Nriagu et al. (1980) found that in Lake Ontario 50-80% of the copper, 20-60% of the Cd, and 60% of the lead were bound to the suspended particulates. Rossman (1981) studied Lake Huron water and found an average total zinc concentration of 310 ng/ℓ and 174 ng/ℓ for filtered water (0.5 μm porosity). Mean total cadmium concentrations were 15.4 ng/ℓ and, for filtered water, 5.10 ng/ℓ. For copper the total was 415 ng/ℓ and filtered, (0.5 μm) 299 ng/ℓ. Rygwelski and Townsend (1982) analyzed 313 water samples from Saginaw Bay, Lake Huron in 1978 and found that, in general, the percentages of samples in which the total metal concentration in water was significantly greater than that of the filtered fraction (.45 μm porosity) were 43% (Zn), 61% (Pb), and 33% (Cu). These studies suggested that lead was highly associated with particulate matter. The Lake Huron studies cited here all showed that copper was predominantly in a dissolved form.

5.2 Concentration of Metals in Particulates

Nriagu et al. (1980) found that the concentrations of copper, cadmium, and lead in the suspended solids taken from different basins in Lake Ontario were generally higher than those in surficial sediments. Average concentrations in the suspended solids were 180 μg/g for copper, 410 μg/g for zinc, 10 μg/g for cadmium, and 190 μg/g for lead. They also observed that the October concentrations of copper, zinc, and cadmium at open lake stations ex-

ceeded the May and June values by factors of two to four. At nearshore stations in October, however, there was a noticeable decrease in particulate metal concentrations. They attributed this seasonal variation to changes in the organic character of the suspended solids. Others have noted a high correlation of trace metals with organic particulates [Suzuki et al. (1979); Gardiner (1974)].

Elzerman et al. (1979) found significant enrichment of Zn, Cd, Pb, and Cu in particulates of the surface microlayer in southern Lake Michigan. Concentrations of metals in these particulates were Zn (50-1800 μg/g), Cd (2-25 μg/g), Pb (30-1900 μg/g), and Cu (50-640 μg/g).

Rygwelski and Townsend (1982) studied particulate trace metals in Saginaw Bay water in 1978. Whole water was separated by filters or screens into dissolved (<.45 μm), and particulate fractions of the following size ranges: .45-10 μm, 10-74 μm, 74-210 μm, and 210-1000 μm. Results (weight metal per dry weight particles) were obtained for the last three size fractions. The 10-74 μm fraction contained the highest concentration of metals (Cu, Zn, and Pb) in the solids. Eutrophic waters of the inner bay often had significantly lower concentrations of metal in the 10-74 μm size fraction than did oligotrophic outer bay waters (Lake Huron). The results of this study are summarized in Table 1.

5.3 Adsorption Isotherm Results

Several empirical adsorption studies have characterized solid-liquid trace metal partitioning in the Great Lakes. Some researchers have examined trace metal partitioning by means of laboratory adsorption tests using lake sediments. Others have filtered or centrifuged lake water samples to isolate

TABLE 1. CONCENTRATIONS OF METAL IN PARTICULATE SIZE FRACTIONS, SAGINAW BAY, LAKE HURON (1978).

Metal	Concentration (μg/g) in Particles		
	10-74 μm	74-210 μm	210-1000 μm
Copper	(3.7 - 1300)* Mean: 410 Median: 300 n: 95	4.8 - 610 Mean: 70.0 Median: 22 n: 101	3.5 - 430 Mean: 95 Median: 31 n: 97
Lead	23.0 - 3300 Mean: 240 Median: 50 n: 100	20.0 - 210 Mean: 46.0 Median: 32 n: 101	4.6 - 540 Mean: 100 Median: 53 n: 85
Zinc	6.3 - 870 Mean: 390 Median: 330 n: 98	95.0 - 430 Mean: 170 Median: 130 n: 101	120 - 650 Mean: 220 Median: 160 n: 102

*Range of metal concentrations found in a given size fraction.

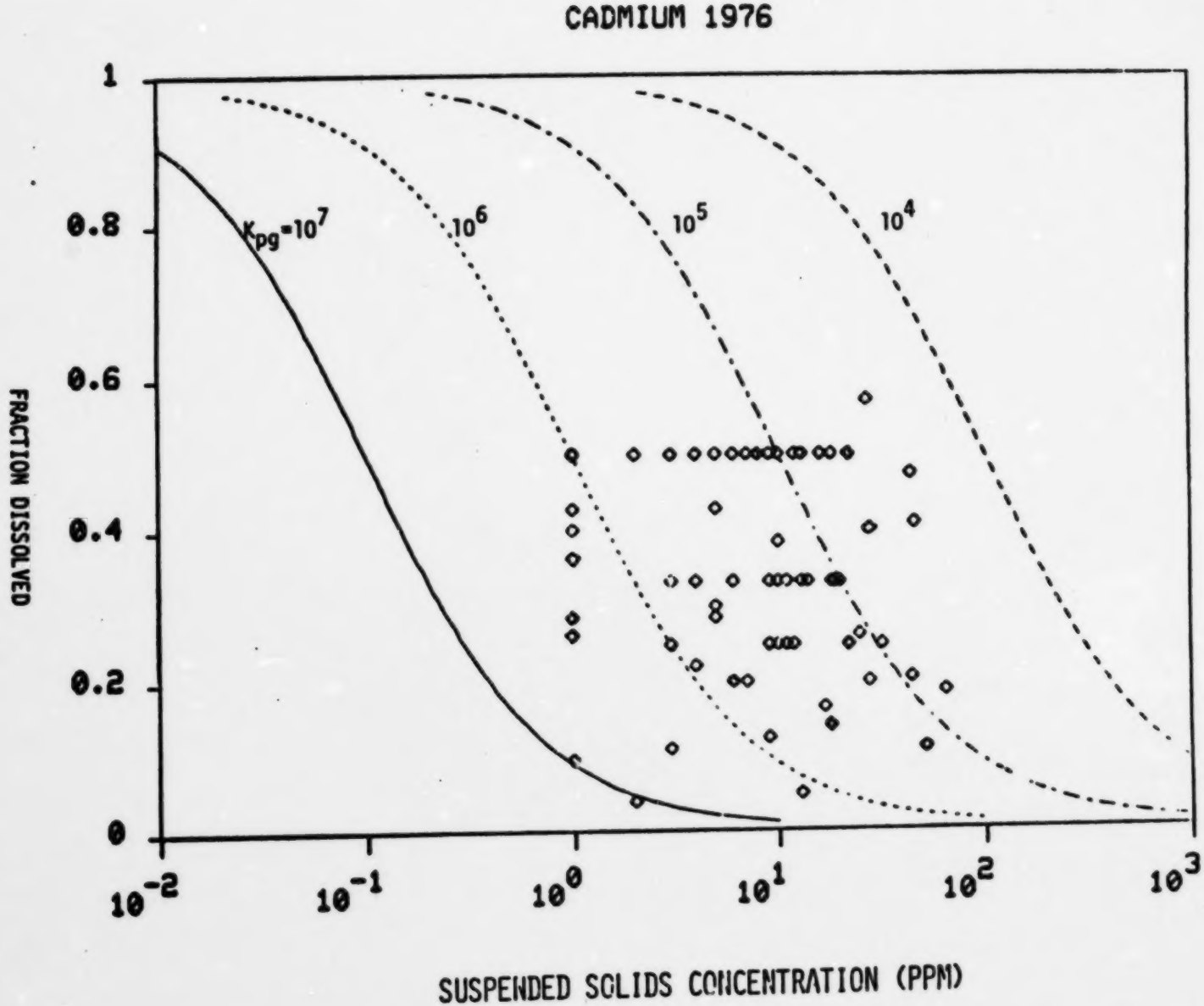
particles. Analysis of the particulate and dissolved concentrations of metals in water enabled them to calculate the percent dissolved and ¶.

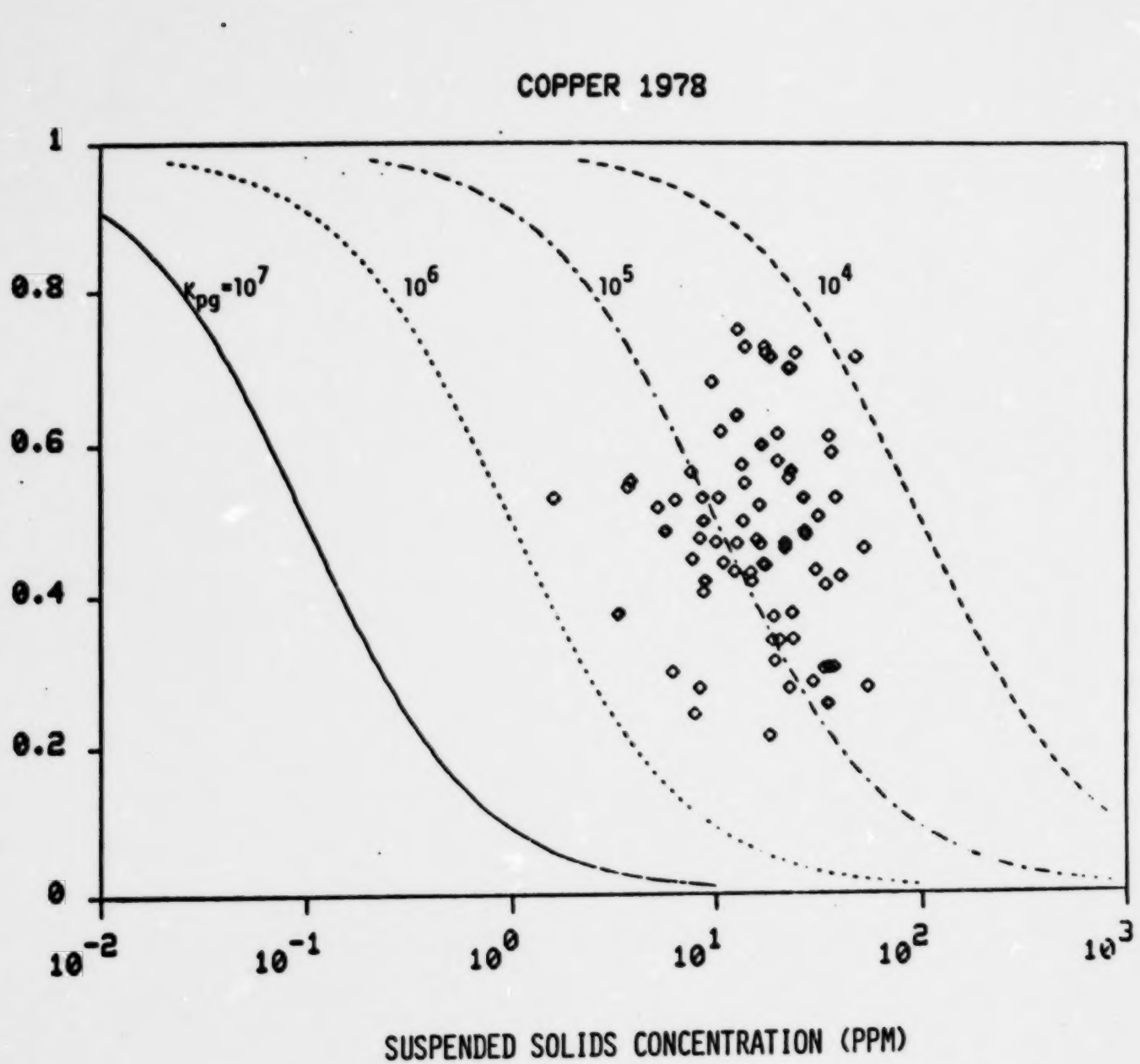
Bahnick et al. (1978) studied the effect of eroded clay bluff materials in Lake Superior water on the partitioning of trace metals. A linear adsorption isotherm characterized copper sorption onto clay bluff materials. Interpolating from this adsorption isotherm, they concluded that each metric ton of eroded bluff material could remove 175 g of copper from the lake water if it contained 10 µg/ℓ of copper.

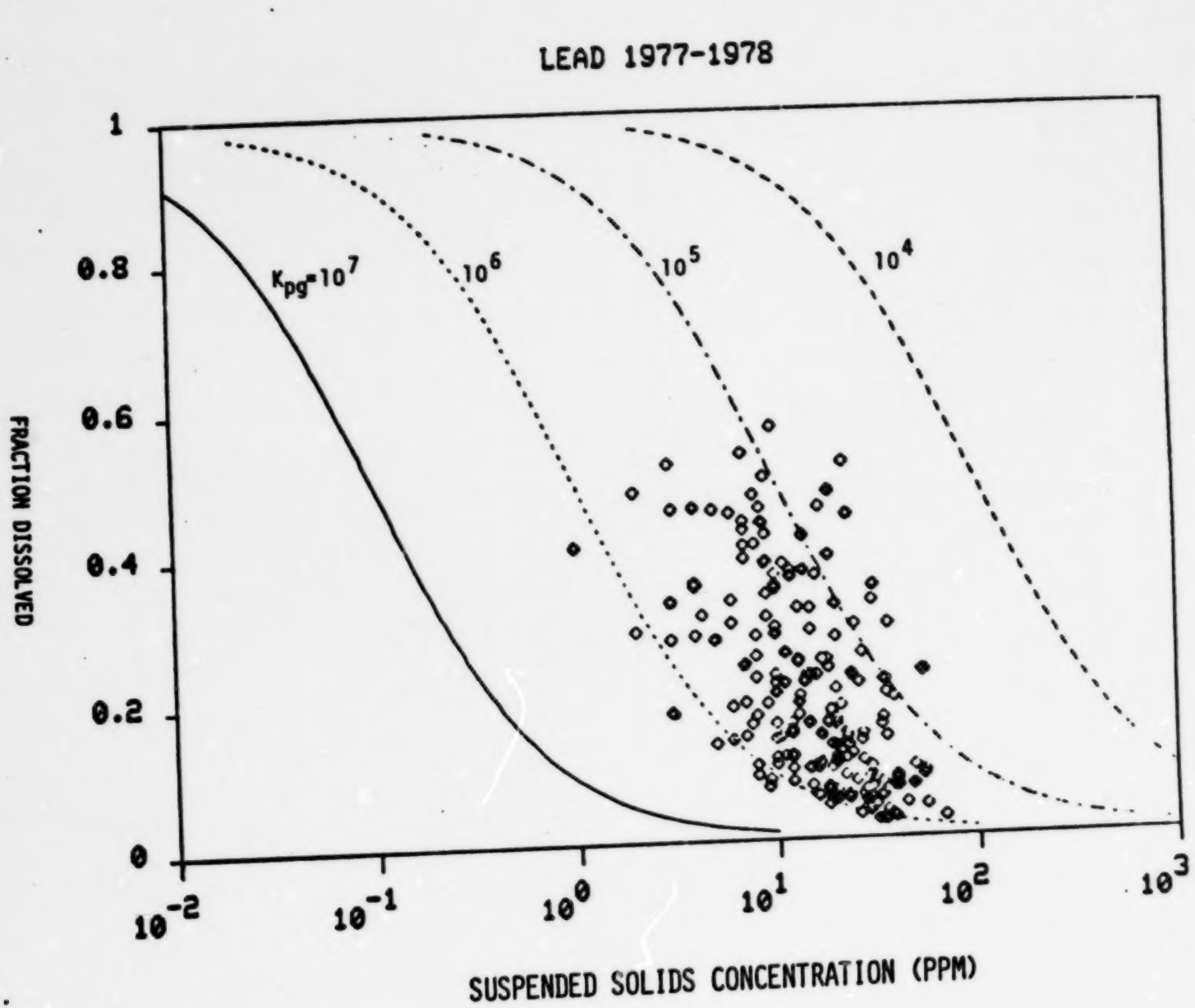
Rygwelski and Townsend (1982) have calculated partition coefficients for cadmium, copper, lead, and zinc from Saginaw Bay, Lake Huron. This system is interesting in that the inner bay is highly eutrophic while the outer bay water is oligotrophic, much like that of open Lake Huron. General partition coefficients, K_{pg}, (as opposed to K_{ps} for specific fractions) were defined for all suspended solids greater than .45 µm.

$$(7)\quad \begin{matrix}\text{(general partition coefficient)}\end{matrix}\quad K_{pg} = \frac{\dfrac{[\text{total metal } (\mu g/\ell)] - [\text{dissolved metal } (\mu g/\ell)]}{[\text{suspended solids kg}/\ell]}}{\text{dissolved metal } (\mu g/kg)}$$

This general partition coefficient was found to vary with location and season in the bay. An increasing trend for K_{pg} was noted from the inner to the outer bay (Figures 1-4). These figures show data from stations throughout the bay. Values were discarded from the original data set if the dissolved metal sample concentration was not less than the corresponding total metal concentration at the 95% confidence level. Some of the vertical non-random alignments of data points in these figures are due to the detection limit for suspended solids. Lines of constant K_{pg} are also plotted on the figures. Partition coefficients for the inner and outer bay are compared in Table 2.


CADMIUM 1976
1
0.8
0.6
0.4
0.2
0
FRACTION DISSOLVED
$K_{pg}=10^7$
10^6
10^5
10^4
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
SUSPENDED SOLIDS CONCENTRATION (PPM)


COPPER 1978
1
0.8
0.6
0.4
0.2
0
FRACTION DISSOLVED
$K_{pg}=10^7$
10^6
10^5
10^4
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
SUSPENDED SOLIDS CONCENTRATION (PPM)


LEAD 1977-1978
1
0.8
0.6
0.4
0.2
0
$K_{pg}=10^7$
10^6
10^5
10^4
FRACTION DISSOLVED
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
SUSPENDED SOLIDS CONCENTRATION (PPM)

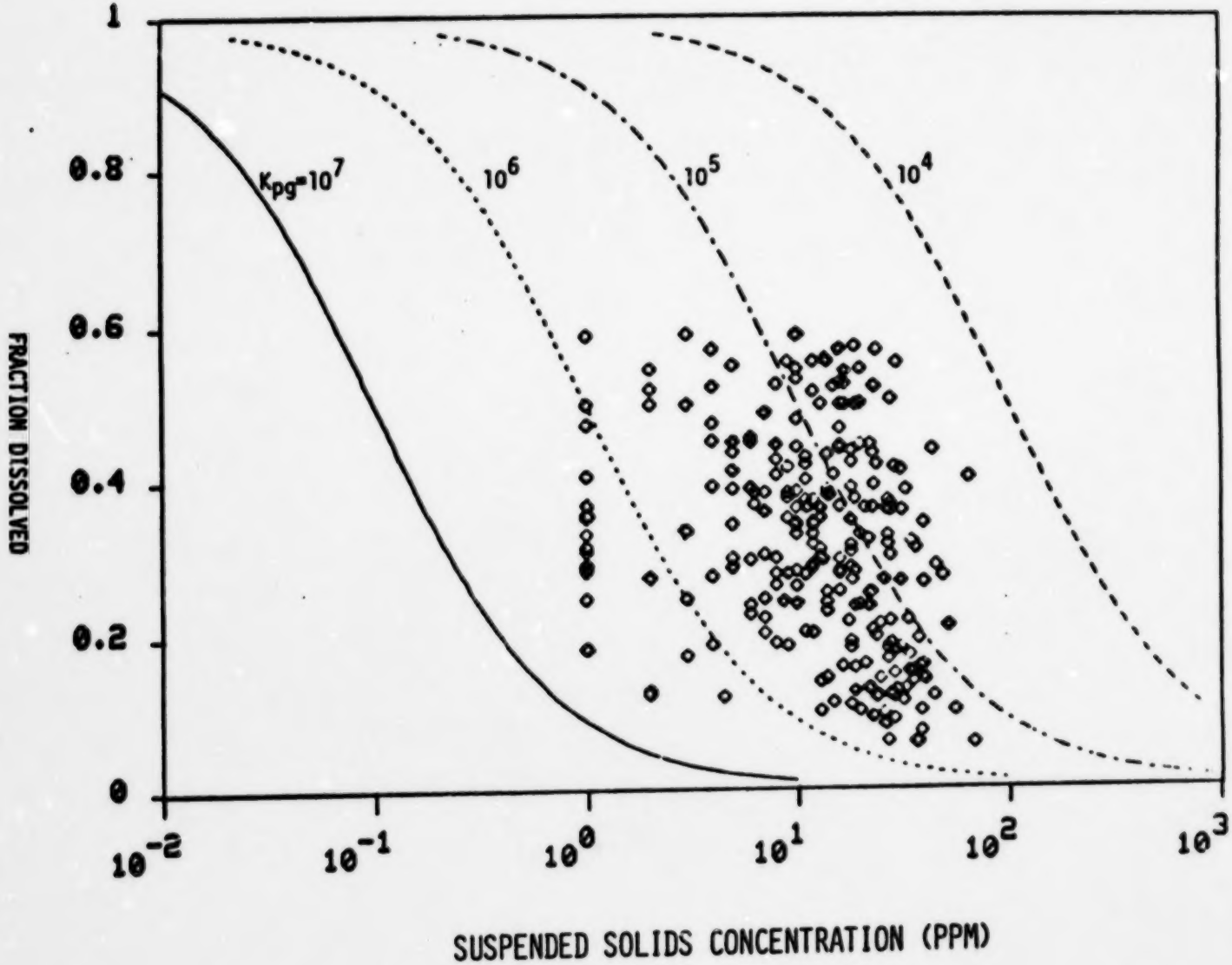

ZINC 1976-1978
1
0.8
0.6
0.4
0.2
0
FRACTION DISSOLVED
$K_{pg}=10^7$
10^6
10^5
10^4
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
SUSPENDED SOLIDS CONCENTRATION (PPM)

TABLE 2. GENERAL PARTITION COEFFICIENT (K_{pg}) DATA FROM SAGINAW BAY, LAKE HURON

Metal	Partition Coefficient Ranges Inner Bay	Partition Coefficient Ranges Outer Bay
Cd	$10^{4.5}$ - $10^{5.5}$	$10^{5.5}$ - $10^{6.5}$
Cu	10^{4} - 10^{5}	$10^{5.2}$ - $10^{5.7}$
Pb	$10^{4.7}$ - 10^{6}	$10^{5.5}$ - $10^{6.3}$
Zn	$10^{4.5}$ - $10^{5.5}$	$10^{5.5}$ - $10^{6.5}$

On the average, copper had the lowest and lead the highest K_{pg} values. Zinc and cadmium coefficients were intermediate and similar to each other. Dolan and Bierman (1982) were able to apply these partition data in mass balance models for trace metals in Saginaw Bay. They determined that large percentages of cadmium (77%), lead (28-38%) and zinc (15-79%) were lost to the sediment each year. Loss of copper to the sediments was estimated to be minimal.

A specific partition coefficient (K_{ps}) also was calculated for each size fraction in Table 1. The fraction which partitioned the highest for all three metals was the 10-74 μm.

6. Conclusions

The theory of trace metal adsorption processes has been discussed and reviewed. Data were presented which show the variability and extent of trace metals uptake by suspended particles in Great Lakes waters. Models which address the fate of trace metals in water must take into account their partition behavior under various conditions of particle size, organic content and concentration. Appropriate sampling techniques and analytical instrumentation are available for further empirical studies of metals partitioning, which are both feasible and necessary. Correlations of data on water and particle chemistry with partition data will help to simplify and improve our understanding of partition phenomena in natural waters.

ACKNOWLEDGEMENTS

Funding for the Saginaw Bay trace metal study was provided by the U.S. Environmental Protection Agency. Laboratory analyses and data management were conducted at the E.P.A. Large Lakes Research Station, Grosse Ile, Michigan. Field operations were also managed at the Grosse Ile lab. I would like to thank V. Elliott Smith for his careful review of the manuscript.

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